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⑦① Applicant: Craig, Dwight R., 7767 E. Quaker Rd., Orchard Park NY 14127 (US)

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⑦② Inventor: Craig, Dwight R., 7767 E. Quaker Rd., Orchard Park NY 14127 (US)

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⑦④ Representative: Kraus, Walter, Dr. et al, Patentanwälte  
Dres. Kraus & Weisert Imgardstrasse 15,  
D-8000 München 71 (DE)

⑤④ Electric energy storage devices.

⑤⑦ This invention relates to novel type electrochemical devices such as capacitors or batteries, among other devices, which have high capacitance or power to volume or weight ratios, or which have other valuable characteristics, and which are characterized by the practical use of one or more phenomena, including pseudocapacitance, "kinetic reversibility" (passage of approximately equal and substantial charge or discharge currents at about the same rate), "coulombic reversibility" (passage of substantially equal numbers of coulombs in the charging and discharging of the device), distinguishable energy states of electrodeposited species on surfaces, creation of surface layers, electrochromic effects, negative differential resistance, and frequency multiplying effects which occur during, or as a result of, the formation or modification of an electrodeposited layer or layers on, or separation of charges in double layers in, one or more electrodes and/or as a result of the reaction(s) occurring between electrode and electrolyte.

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ELECTRIC ENERGY STORAGE DEVICESBACKGROUND OF THE INVENTION

The history of electrochemical energy storage devices, especially capacitors and batteries, has involved attempts  
5 to reduce the size, including both weight and volume, and to increase the electrical energy storage capacity while at the same time increasing the voltage required for dielectric breakdown. The occurrence under certain conditions of large electrochemical capacitance including  
10 pseudocapitance is well established, but prior to this invention, no significant practical devices or applications having a high degree of "kinetic reversibility" have been made. Recent technological advances in capacitors have included aluminum electrolytic capacitors,  
15 tantalum capacitors, and ceramic among others, all of which are film-type capacitors. Recent advances in battery design have included improvement in life, efficiency and energy density by making available improved lead acid,

nickel cadmium, nickel zinc, and various primary cells all of which are inherently over-voltage devices limited by electrode polarization. However, although many of the devices embracing the recent technological advances have  
5 filled a need, there continues to be a requirement for efficient high power density devices which withstand the rigors of continuous use and virtually unlimited cycling in electrical circuits. This invention provides such devices which shall be referred to herein as Supercapacitors.

10

SUMMARY OF THE INVENTION

This invention relates to a novel type of electrochemical device such as a capacitor or a battery and more particularly to the practical use of an electrochemical system exhibiting a high degree of pseudocapacitance,  
15 "kinetic reversibility," and/or "coulombic reversibility," with which is sometimes associated a capacitance, among other characteristics, arising from the passage of charge that accompanies the change of potential of a suitable electrode. The devices of this invention also permit  
20 taking advantage of the energy storage capacity formed by a pair of spaced electrodes immersed in an ionized electrolyte (that is, double-layer capacitance and the geometric dielectric capacitance).

DESCRIPTION OF THE INVENTION

The Supercapacitor is an electrochemical cell or combination of cells comprising two electrodes, an electrolyte, and a container therefore, wherein the electrodes  
5 are composed of one or more of the following materials:  
the oxides of ruthenium, tantalum, rhodium, iridium, cobalt, nickel, molybdenum, tungsten, and vanadium, the sulfides of iron and lead, and their metals and their sulfides, hydrides, nitrides, phosphides, and selenides,  
10 and mixtures thereof; and wherein the electrolyte may be acidic or basic or neutral, aqueous or nonaqueous, such as sulfuric acid or potassium hydroxide or sodium sulfate; and wherein a suitable container is used to house the preceding components. In addition, the Supercapacitor may  
15 advantageously employ a separator between the electrodes. Ion permeable membranes, hydrophilic plastic films, glass, paper, felt, and cellulose are all suitable depending on the particular application and device. Current collector grids or meshes may be employed in the electrode  
20 assembly if desired.

The Supercapacitor is an electrochemical cell or combination of cells characterized by 1) the formation and/or reactivity of an electrodeposited layer or layers on on

or more electrodes, and/or by 2) the type of reaction occurring between electrode and electrolyte, and/or by 3) the separation of charges across double layers. These characteristic processes occur in a potential range throughout which no continuous reaction occurs of an electrode or electrolyte in the system. They give rise to one or more of a multiplicity of phenomena including, but not limited to, pseudocapacitance, "kinetic reversibility," "coulombic reversibility," distinguishable energy states of electro- deposited species on surfaces, creation of surface layers, electrochromic effects, negative differential resistance, and frequency multiplying effects. These characteristic processes are useable in many ways, some of which will be described in more detail hereinafter and in the examples and description of the drawings.

A large family of devices is conceived which employ these basic characteristic processes. Examples of these are electronic-capacitor-like devices; battery-type devices; passive negative differential resistance devices; passive frequency conversion devices; electrochromic devices; data processing memories; gaseous, liquid, and solid material separation devices and systems; and passive devices exhibiting constant reactance versus frequency, which devices may utilize one or more of the characteristics described in the previous paragraph.

The electrochemical cells used for these applications may be produced in various forms, such as plane electrode cells; "jelly-roll" cells; porous electrode cells; slurry systems; fluidized-bed electrodes; endless belt electrodes; 5 transparent or opaque electrodes and housings; liquid, solid, or gaseous electrolytes; etc., depending on the nature of the device. Furthermore, in several of the foregoing devices of this invention which take advantage of the electrodeposition or reaction that occurs at under- 10 potential, I have found that the elements of the metals disclosed may be used as electrodes. For example, in data processing memory device applications, metals such as platinum, gold, or iridium might be preferred electrode materials because they exhibit a one-to-one relationship between the 15 metal adsorbent atoms and the hydrogen (or other) electrodeposited atoms, thereby allowing for a memory density approaching the surface density of metal atoms in the surface (which is on the order of  $10^{15}$  per square centimeter). Also, in solid material separation devices such as in the 20 separation of metallic lead, the lead can be electrodeposited from aqueous solution (lead chloride) onto a metallic substrate electrode, preferably gold, such electrodeposition of lead being preferential to other ions and reversible with respect to voltage on this electrode, 25 thereby permitting separation or refining of lead with the

use of minimal amounts of electrical energy.

DESCRIPTION OF DRAWINGS

Figure 1 is a voltammogram showing oxygen and hydrogen electroadsorption and electrodesorption on platinum surfaces at potentials less than those required for gas evolution.

Figure 2 is a voltammogram in aqueous solution of ruthenium oxide, an electrode material preferably employed in this invention.

10      Figure 3 is a voltammogram in aqueous solution of a mixture of ruthenium and tantalum oxides which is a mixed metal oxide electrode material also advantageously employed in this invention.

15      Figure 4 is still another voltammogram in aqueous solution of another material, namely, molybdenum oxide, which is also employed in certain devices of this invention.

Figure 5 is a voltammogram of tungsten oxide in aqueous solution.

20      Figure 6 is a voltammogram of nickel oxide in aqueous solution.

Figure 7 is a monopolar parallel plate structure capacitor in accordance with this invention.

Figure 8 is a monopolar "jelly-roll" structure capacitor in accordance with this invention.



Figure 9 is a more detailed view of the basic structure of the capacitor of this invention which is a preferred embodiment.

Figure 10 is a diagrammatic sketch of a battery of this invention.

# DETAILED DESCRIPTION OF THE INVENTION

The phenomena which are so novelly employed in the devices of this invention are the result of certain reactions which occur in some electrochemical cells. An example of pseudocapacitance occurs in the deposition and ionization of hydrogen and oxygen on platinum surfaces at potentials less than those required for gas evolution. The voltammograms of Figures 1 through 6 were obtained by use of the procedure described generally in Modern Electrochemistry by Bockris and Reddy on page 1316.

Figure 1 (not an actual voltammogram) depicts oxygen electroadsorption (area A), oxygen electrodesorption (area B), hydrogen electroadsorption (area C), and hydrogen electrodesorption (area D).

The area between the curve and the x-axis represents the charge delivered to or accepted from the electrode ( $Q = \int i dt$ ). In this case, as the voltage is cycled, the electrode is alternately charged and discharged, first as hydrogen is electroadsorbed and electrodeposited, then as

oxygen is electroadsorbed and electrodesorbed. The name given to the charge/discharge phenomenon is "pseudocapacitance," since it behaves like a capacitance, but the storage of charge involves a Faradaic process, rather than an electrostatic one. Electrochemistry literature tells us that this pseudocapacitance is not a real capacitance, since it will not hold a charge, but this invention makes use of it as a storage means. (See Bockris and Reddy, Modern Electrochemistry, P. 1027.)

10 In the case referred to above (Figure 1), the coulombic charge ( $Q = \int i dt$ ) during electroadsorption in the oxygen region is substantially the same as the coulombic discharge during electrodesorption. The same is true for the hydrogen region, taken separately from the oxygen and, 15 of course, for the total reaction, taken over the voltage range 0 to approximately 1.3 volts RHE. This balance of coulombic charge and coulombic discharge shall be referred to herein as "coulombic reversibility."

In Figure 1, the electroadsorption and electrodesorption of oxygen occur at different voltages, and 20 their current traces are of different shapes. The electroadsorption and electrodesorption of hydrogen, on the other hand, occur at approximately the same voltage and produce curves that are approximate "mirror images." Figure 2 is 25 a voltammogram of a preferred electrode material of this

invention, i.e., ruthenium oxide. From Figure 2 it can be seen that all sections of the curve show approximate "mirror images" with respect to the voltage axis. Representative "mirror images" in this context are shown in Figures 2 through 6. This "mirror image" phenomenon shall be referred to herein as "kinetic reversibility" while the non-"mirror image" such as the oxygen electroadsorption-desorption in Figure 1 shall be referred to as "kinetic nonreversibility" or partial reversibility. Systems that are "kinetically reversible" show very high electrical efficiency, since they return charge at the same voltage at which they receive it. Systems that are "kinetically nonreversible" are less efficient, since they are charged at a different voltage than that at which they are discharged.

Referring again to Figure 1, in the hydrogen region we see three current peaks between the voltages of 0.4 and 0.0 RHE, corresponding, it is believed, to the electroadsorption and electrodesorption of hydrogen at (probably) different sites on the platinum surface. We also see less-well-defined peaks in the oxygen region where it is believed that oxygen is similarly adsorbed and desorbed. Coincident with these reactions is observed a change of entropy and a heat of adsorption or desorption of the

hydrogen and oxygen and of other species which may occupy the site, such as organic impurities or water molecules. Thus there are in these reactions distinguishable energy states of various electrodeposited species on the surfaces of the substrates.

Further to analyses relating to Figure 1, it is now believed that the electrosorption of hydrogen on platinum produces a surface monolayer of hydrogen, while the electrosorption of oxygen can produce multiple surface layers of oxygen or oxide.

In the creation of some surface layers, such as oxides on ruthenium, under the proper conditions, we observe a change in the optical appearance or reflectivity of the surface.

Referring once more to Figure 1, we observe that, for example, the portion of the hydrogen desorption curve at about 0.35 volts RHE shows a reduction of current with an increase in voltage. This represents a negative differential resistance characteristic which occurs in the systems of this invention. Also, the area at 0.0 to 0.4 volts RHE shows three cycles of current for one-half cycle of voltage, which frequency-multiplying characteristic occurs in the systems of this invention.

The unique characteristics exhibited in the systems of this invention, including "kinetic reversibility,"

"coulombic reversibility," distinguishable energy states of electrodeposition, creation of surface areas, electrochromic effects, negative differential resistance, and frequency multiplying effects are employed in the electrical  
5 energy devices referred to herein.

In order for this invention to be more readily understood and to describe the many variations that may be employed in each of the components, this invention will now be detailed using a capacitor as an example; however,  
10 this is not to be construed as limiting this invention.

#### THE ELECTRODE

The electrodes of this invention, their composition, preparation, and assembly in the Supercapacitor devices of this invention are critical to obtaining the superior performance in electrical and physical characteristics of the  
15 devices to be exemplified hereinafter. I have found that in order to maximize the reduction in size, including volume and weight ratios, to the energy storage capacity and to optimize the combined effects of pseudocapacitance, double-layer capacitance and "kinetic reversibility," it  
20 is desirable to employ an electrode material having a voltammogram of substantially symmetrical current traces in the oxidation and reduction cycles. Materials that may advantageously be employed are ruthenium oxides and

mixtures of ruthenium with tantalum and/or iridium, preferably a 50-50 mole percent  $\text{RuTaO}_x$  or such a mixture with amounts of iridium such as  $\text{Ru}_{0.5}\text{Ir}_{0.25}\text{Ta}_{0.25}\text{O}_x$ . Other electrode materials such as previously described  
 5 may be employed, it being preferable that their voltamograms show substantial "kinetic reversibility" such as that shown in Figures 2, 3, 4, 5, or 6.

When employing ruthenium as the electrode material, the ruthenium content may be varied over wide ranges as  
 10 shown when mixed with, for example, tantalum, or iridium. The following data in Table I illustrates a measured variation in capacitance per unit geometric area against mole percent of ruthenium in the electrode material when mixed with tantalum.

15

TABLE I

Capacitance Versus Composition

| <u>Mole % <math>\text{RuO}_2</math> in <math>\text{Ta}_2\text{O}_5</math></u> |    | <u>Capacitance (<math>\text{F}/\text{cm}^2</math>)</u> |
|---|----|--|
|   | 20 | 0.045  |
|   | 25 | 0.1  |
| 20  | 40 | 2.0  |
|   | 50 | 2.8  |
|   | 60 | 1.6  |
|   | 75 | 0.8  |

The porosity of the electrode is another factor that  
 25 contributes to optimization of results for devices of this

invention. In general, porosity is desirable in order to maximize the energy storage density, or capacitance per unit volume. However, proper control of the porosity will also allow control of the internal resistance and of the reaction rate (by controlling the access time of the electrolyte to the electrode), thus providing a measure of control over the capacitance versus frequency characteristic. This can be controlled to the extent of providing capacitance which varies inversely with frequency, thus allowing production of a constant reactance device, as mentioned hereinbefore.

The thickness of the oxide coating is still another factor that affects the performance and characteristics of the Supercapacitors of this invention. Generally, the capacitance varies with the thickness of the ruthenium oxide coating so that by varying the thickness of the coating, the capacitance per unit area may be controlled. Using the thermal oxidation technique (see H. B. Beer, South African Patent 662.667 (1966) and 680.034 (1968)) a thick and uniform ruthenium oxide formation was obtained. This coating was tenacious and further did not exhibit any flaking or other undesirable characteristics.

In addition, I have found that the purity of the metals or metal compounds used in the preparation of the electrodes can have a significant effect on the performance

of the device. For example, it is obvious that the wrong type of metallic impurity in a capacitor or other device using a metal electrode would produce a galvanic corrosive action which would deteriorate the electrode and probably  
5 increase the leakage current of the device. In general, I prefer a purity of 99 percent or better, but certain systems can tolerate high percentages of impurities without detrimental effect. In some cases, additives can even be beneficial, as in the case of, e.g., tantalum oxide  
10 addition to ruthenium oxide (see Table I). In this case, addition of 50 percent tantalum oxide maximized the specific capacitance of the device.

Various processes and techniques may be employed in the preparation of the electrode. Among those methods  
15 which I have found satisfactory are: thermal preparation of the selected material, e.g., ruthenium-tantalum mixed oxides; electrochemically generated ruthenium oxide; and pressed pellet electrode preparation, including the use of binders, e.g., teflon powder, if desired. Other  
20 methods of preparing a ruthenium oxide electrode may be employed, for example, precursor or impregnation techniques. In the examples which follow, specific details will be given concerning the preparation of electrodes in connection with the data obtained in specific experiments  
25 and with preferred embodiments of this invention.



### THE ELECTROLYTES

The electrolytes which may be used in the Supercapacitor of this invention may be acidic, alkaline, or neutral, aqueous or nonaqueous. I have used, successfully, electrolytes varying in pH from (-) 1 to (+) 14, taking into account, of course, the chemical stability of the electrode in the electrolyte. pH affects the specific capacitance of the device, with the amount varying with the electrode and with the electrolyte. Examples of electrolytes employed are: NaOH, H<sub>2</sub>SO<sub>4</sub>, KOH, HCl, NaClO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, and K<sub>2</sub>SO<sub>4</sub>. Solid or gaseous electrolytes may, of course, also be used provided the active ions are compatible with the electrode adsorption or reaction process.

### THE CONTAINER AND ASSEMBLY OF THE SUPERCAPACITOR

Figure 7 illustrates one of many possible configurations of a monopolar type of capacitor that can be made using concepts described in this invention. Electrodes, of various sizes and shapes, may be used, having been previously coated with active materials such as ruthenium oxide. These electrodes are provided with conductive tabs for current conduction to and from the electrodes. The electrodes are then stacked, alternating electrode (1) which may be positive and electrode (2) which is negative and using a suitable separator (3) to prevent shorting of

electrodes (1) and (2). The lead tabs (4) are brought outside the casing (5) through a suitable hole (6) in the end cap (7), and tabs (4) from the multiple electrodes (1) and (2) may be gathered together by welding. After insertion  
5 of the electrolyte (8), the assembly may then be drawn lightly together by use of a turnbuckle-type of casing (5) and recesses (10). Electrolyte leakage may be prevented by the use of a suitable sealant (9). This assembly may be hooked up in a plurality of units to produce a capacitor  
10 of any given capacity.

Figure 8 represents another possible configuration of a monopolar type of capacitor, popularly termed a "jelly-roll" type. Here two electrodes (1) and (2), coated with an appropriate active material such as ruthenium oxide (not  
15 shown) are prevented from shorting by interleaving a suitable separator (3), and are rolled up in "jelly-roll" fashion as shown. Tabs (4) are extended from each of the electrodes through the casing (5), and after insertion of a suitable electrolyte (8), the holes (6) are plugged with  
20 a suitable sealant (9).

The Supercapacitors of this invention have much larger capacitance per unit volume than aluminum electrolytic capacitors. For example, an experimental capacitor produced in accordance with this invention and of the design  
25 shown in Figure 9 of 6 volts and 10,000 ufd was 1/10 the

physical size of a standard commercial aluminum electrolyte capacitor of the same voltage and capacitance. Another model of the same design yielded 1/30 the physical size of the commercial capacitor. To achieve the high energy density capacitor (small volume and light weight) it is preferable to optimize not only the electrode material, the electrolyte, and the separators, when used, but also the physical configuration, stacking, end terminals, and the container or case, thereby permitting improvement in physical size.

Figures 7, 8, and 9 illustrate various configurations for capacitors of this invention. In the Supercapacitor shown in Figure 9, the electrodes (1) and (2) are 10 mil. thick substrate titanium coated with  $\text{RuTaO}_x$  and the spacer-gaskets (11) are 15 mil. thick Viton. This is pressure sealed, preventing electrolyte leakage and shunt current losses. The case sealant (9) is electrolyte resistant compound such as epoxy resin coated over the assembled stack. The case cylinder (5) may be a plastic such as Kovar, polyethylene, or polypropylene. The end caps (7) are copper and the wires are spot welded to the two end electrodes (1) and (2).

The assembly procedure comprises stacking (a) the oxide coated electrodes which are oxide free on their edges so that they will seal when assembled, (b) the end

electrodes which are oxide coated on one side and which  
hav their lead wires spot welded, and (c) the Viton gas-  
kets. The stack so formed is immersed in the electrolyte  
under vacuum. The stack is removed from the electrolyte  
5 pressure sealed. The stack is then coated with insulator  
compound such as epoxy resin by forcing the resin through  
the opening (13) and out through the exit (14).

The concept of this invention may be employed, for  
example, in batteries for use in powering pacemakers for  
10 implantation in humans where regulation of heartbeat is  
required. Since this battery is electrically rechargeabl ,  
it would be recharged by inductance from outside the body,  
thus permitting recharging without removal from the body.  
(Present batteries for this use are not rechargeable elec-  
15 trically and must be replaced about every five to seven  
years by a surgical process.) Further, this recharging  
would be done at periods shorter than the above-mentioned  
five to seven years, allowing much smaller batteries to  
be used. Further, with batteries of this invention, ex-  
20 tremely long life and a very great number of cycles can  
be realized, thus eliminating the need for any further  
surgery, once the initial implantation is accomplished.  
This battery is particularly well suited to this applica-  
tion because f its small size, its long cycle lif , and  
25 its rechargeability.

In another application, this battery would be used for utility load-levelling by charging a great number of cells (connected in a suitable series-parallel arrangement) at night over, say, a ten-hour period when the load demand in a utility power-generation station is low. These batteries would then be discharged at the peak load demand hours of the day, thus allowing a relatively constant power-generation level to be used by the utility. Other advantages also derive from this practice and are well-known to those acquainted with load-levelling technology. This battery is particularly well-suited to this technology because of its high charge-to-discharge efficiency and its very long cycle life.

Figure 10 illustrates a typical one-cell battery of this invention. Electrodes (1) and (2) are, in this case, porous slugs of ruthenium oxide powder, prevented from shorting one to the other by a suitable separator, and enclosed in a casing (in this case made of an insulating material, although the electrode and leads could easily be insulated from the casing if the casing were made of metal or other conductive material). Either electrode can be considered as the positive electrode with this design, and the battery can be charged alternately in one polarity and then in the opposite polarity without damage.

A list of characteristics of the battery of this invention is given below:

1. A very high round trip (charge-discharge) efficiency
- 5      2. Very long life
3. Very great cycle life
4. High power density
5. Very high charge and discharge rates
6. Capacity substantially invariant with high dis-
- 10      charge rates
7. Shallow and deep discharge capability without affecting lifetimes
8. Reasonable energy density
9. Electrically rechargeable (secondary type)
- 15      10. Simple construction, black box type

Table II gives the performance characteristics of Supercapacitors made as described above. The following examples are given to further illustrate this invention; however, they are not intended to limit the scope thereof.

TABLE II

|                | <u>Example I</u>                     | <u>Example II</u>                    |
|----------------|--------------------------------------|--------------------------------------|
| Device Type    | Capacitor                            | Capacitor                            |
| Electrode      |                                      |                                      |
| 5 a. Form      | Thermally formed                     | Pellet                               |
| b. Composition | TaRuO <sub>x</sub>                   | RuO <sub>2</sub>                     |
| Electrolyte    | 3.5 M H <sub>2</sub> SO <sub>4</sub> | 3.5 M H <sub>2</sub> SO <sub>4</sub> |
| Polarity       | Bipolar/Nonpolar                     | Single Cell/Nonpolar                 |
| Volume         | 5.0 cm <sup>3</sup>                  | 0.5 cm <sup>3</sup> (appr.)          |
| 10 Capacitance | 10,000 ufd                           | 65 Fd                                |
| Tolerance      | ± 10%                                | ± 5%                                 |
| Voltage        | 6 V                                  | 1 V                                  |
| ESR            | 80 mΩ                                |                                      |
| Assembly       | See Figure 9*                        | See Figure 10                        |
| 15 a.          | 10 mil. gaskets                      | Separator                            |
| b.             | 1 mil. Ti substrates                 |                                      |
| c.             | Screw assembly                       |                                      |

\*Figure 9 shows a 3 volt capacitor of similar construction.

20 THE ELECTRICAL AND OPERATING CHARACTERISTICS  
OF DEVICES OF THIS INVENTION

Th electrical characteristics of the rechargeable electrochemical cells of this invention are more readily understood by reference to the drawings in Figures 2

through 6 which show voltammograms of various electrode/  
electrolyte combinations or systems embraced within this  
invention. Once the device has been charged by applying  
a voltage to its terminals and the device is disconnected  
5 from its voltage source, no current will be flowing and  
the voltage of the positive electrode will be at the high  
voltage end of the curve as shown in Figure 2 (point A).  
When applying an electrical load across the terminals,  
current flows and traces the path of the curve in the  
10 lower section below the horizontal axis along the path  
A, B, C, D, until the electrode is fully discharged which  
is shown at point D.

When charging the device, the current for the positive  
electrode traces the curve in the upper section above the  
15 axis along the path D, E, F, A. The other electrode has  
substantially the same electrical characteristics, which  
can be depicted in a similar manner, except that the  
current flow is the opposite, that is, discharging along  
path G, H, E, D and charging along path D, C, J, G. Thus  
20 the devices of this invention possess the unique feature  
of maximizing the use of "kinetic reversibility." This  
is also shown by Figure 2 because the amount of current  
flowing during charge of the device is substantially the  
sam , but of opposite sign, as the current fl wing during  
25 discharge of the device at th sam p tential. This is



especially true for those systems having curves in the charge/discharge cycle which have the forms of closed "mirror images." The ideal system for an electronic capacitor is depicted as the broken line rectangle for Figure 2  
5 for the electrode/electrolyte system described. It can readily be seen that the actual curve closely approximates the ideal.

The devices of this invention which employ "kinetic reversibility," have the additional advantage that the  
10 capacitance of an electronic capacitor (or the capacity of a battery) can be controlled by the electrical or photoactive bias (e.g., D.C. working voltage level) impressed on the device. For example, in referring to Figure 4, the instantaneous capacitance depends on the height of the curve  
15 above the x-axis at the instantaneous voltage. Since this height varies with the position along the x-axis, it can be seen that the capacitance can be controlled by operating the device at a higher or lower voltage. This voltage level can be effected by the use of any of a number of features  
20 such as multiple electrodes or electrodes of different effective reactivity (for example, different volumes or surface areas).

The electrochemical reactions that take place in the metals from the materials of this invention are not fully  
25 known, however, some of the electrode materials known to

be capable of existing in a plurality of oxidation states such as the oxides of ruthenium, tungsten, molybdenum, and cobalt are among those which are preferred for capacitor devices. It is important in operating the devices of this invention not to apply a voltage across its terminals that causes continuous reaction of the electrolyte and to keep it below the range where there is any significant amount of evolution of oxygen or hydrogen at the electrodes or dissolution of the electrodes themselves.

10        Although my invention has been described with respect to specific examples, illustrations, and certain preferred embodiments thereof, I do not intend that my invention should be thereby construed as being limited in scope except as expressly defined in the appended claims.

I CLAIM:

Claim 1

An electrical energy storage device which is a rechargeable electrochemical cell or plurality of cells comprising at least two electrodes, an electrolyte, and a container therefore wherein at least one electrode is characterized by having as its active electrochemical material a metal or a compound of such metal or mixture thereof having a voltammogram whose charge/discharge curve trace sections are in substantially "mirror image" form when used in the presence of the electrolyte.

Claim 2

An electrical energy storage device in accordance with Claim 1 wherein both electrodes are characterized by having their active electrochemical materials composed of the same substance.

Claim 3

An electrical energy storage device in accordance with Claim 1 wherein the active electrochemical material is composed of an oxide or a mixture of oxides of the same or of different metals.

Claim 4

An electrical energy storage device in accordance with Claim 3 wherein the oxide is of ruthenium.

Claim 5

An electrical energy storage device in accordance with Claim 3 wherein the oxide is a mixture of ruthenium and tantalum.

Claim 6

An electrical energy storage device in accordance with Claim 3 wherein the oxide is of molybdenum.

Claim 7

An electrical energy storage device in accordance with Claim 3 wherein the oxide is of tungsten.

Claim 8

An electrical energy storage device in accordance with Claim 1 wherein the active electrochemical surface is a metal.

Claim 9

An electrical energy storage device in accordance with Claim 8 wherein the metal is iridium.

Claim 10

An electrical energy storage device in accordance with Claim 1 wherein the electrolyte is a liquid.

Claim 11

An electrical energy storage device in accordance with Claim 1 wherein the electrolyte is a solid.

Claim 12

An electrical energy storage device in accordance with Claim 10 wherein the liquid is an aqueous inorganic acid.

Claim 13

An electrical energy storage device in accordance with Claim 12 wherein the aqueous inorganic acid is sulfuric acid.

Claim 14

An electrical energy storage device in accordance with Claim 10 wherein the liquid is an aqueous base.

Claim 15

An electrical energy storage device in accordance with Claim 14 wherein the aqueous base is caustic soda.

Claim 16

An electrical energy storage device in accordance with Claim 10 wherein the liquid is an aqueous neutral salt.

Claim 17

An electrical energy storage device in accordance with Claim 16 wherein the aqueous neutral salt is sodium sulfate.

Claim 18

A battery in accordance with Claim 1.

Claim 19

A capacitor in accordance with Claim 1.

Claim 20

An electrical energy storage device in accordance with Claim 1 wherein the voltammogram has a "mirror image" charge/discharge trace of substantially varying height at different voltages.

Claim 21

The process for storing electrical energy in an electrochemical device comprising positive and negative electrodes, electrolyte, and a container therefore wherein at least one of the electrodes is composed of a material selected from the group consisting of the oxides of ruthenium, rhodium, tantalum, cobalt, iridium, molybdenum, nickel, vanadium, and tungsten, their metals, sulfides, hydrides, nitrides, phosphides, selenides, the sulfides of iron and lead, and mixtures thereof, said materials having a voltammogram whose charge/discharge curve trace sections are in substantially "mirror image" form which comprises:

1. charging the device by introducing an electrical current through the electrodes,
2. maintaining the potential on the device below the continuous reaction voltage of the system employed, until the desired charge is obtained, ,
3. discharging the stored electrical energy in the system designed for the desired application or use of the electricity.

Claim 22

The process of Claim 21 comprising repeating the charge cycle after discharge in order to recharge the device for its continuous or subsequent use.

Claim 23

The process of Claim 21 wherein the said materials exhibit pseudocapacitive characteristics.

Claim 24

The process of Claim 21 wherein the voltammogram has a "mirror image" charge/discharge trace of substantially varying height at different voltages, and wherein the device is operated at different voltage levels to control the electric energy storage capacity.

Claim 25

An electrical energy device which is a rechargeable electrochemical cell or plurality of cells comprising at least two electrodes, an electrolyte, and a container therefore wherein at least one electrode can be characterized by having as its active electrochemical material a metal, a metal compound, or a mixture of metals, and/or compounds which, in combination with the electrolyte, exhibits one or more of the characteristics of pseudocapacitance, "kinetic reversibility," or "coulombic reversibility."

Claim 26

An electrical energy device in accordance with Claim 25 wherein at least one electrode, in combination with a suitable electrolyte, can be characterized by having a combination of pseudocapacitance and "kinetic reversibility."

Claim 27

An electrical energy device in accordance with Claim 25 wherein at least one electrode, in combination with a suitable electrolyte, can be characterized by having a combination of pseudocapacitance and "coulombic reversibility."



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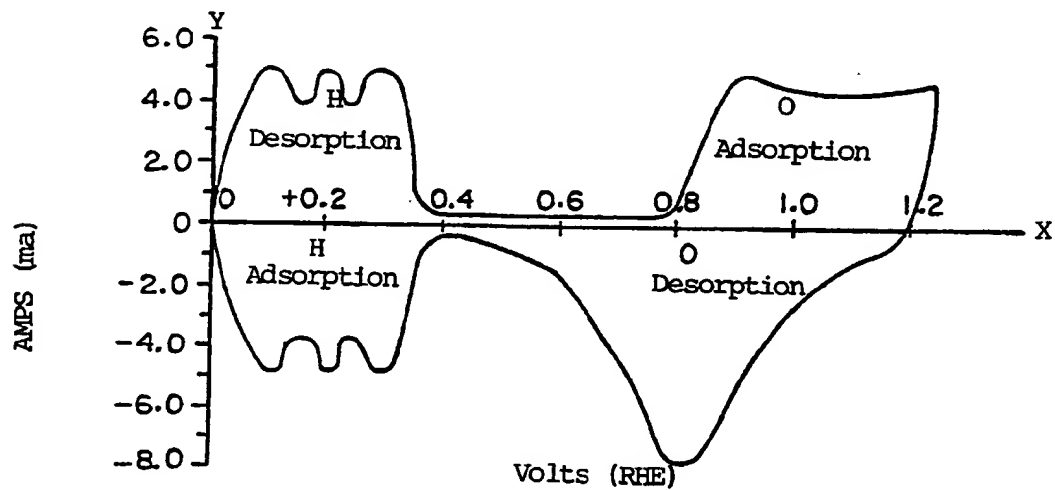


FIG. 1

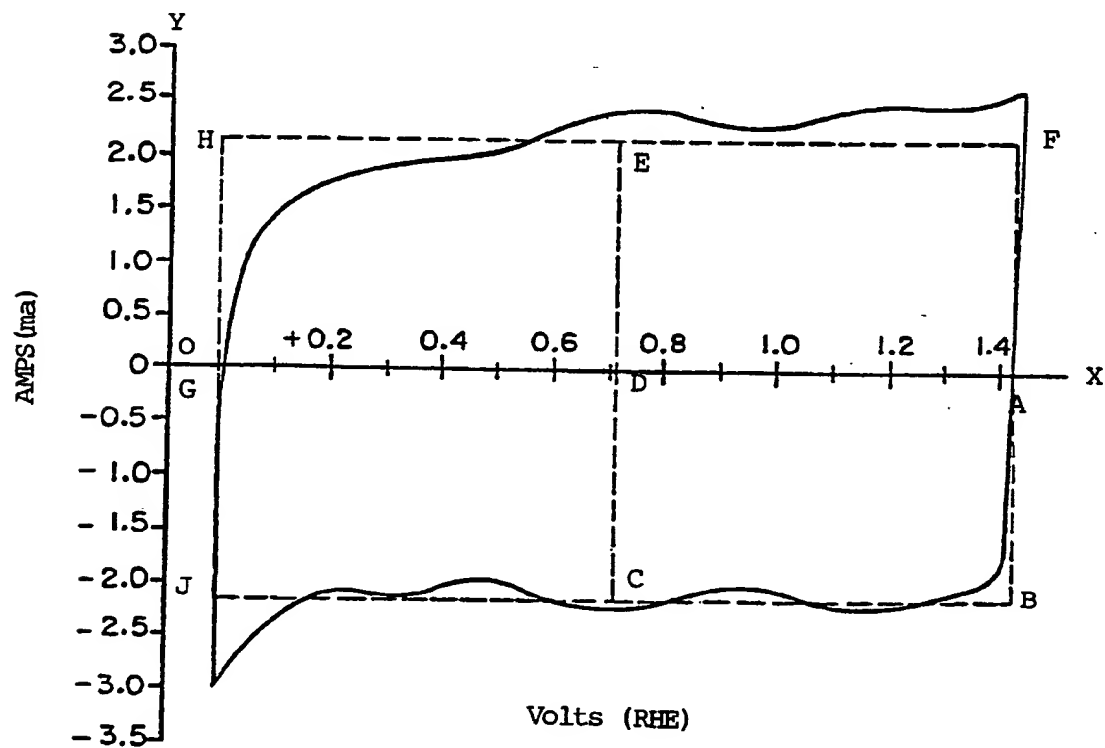


FIG. 2

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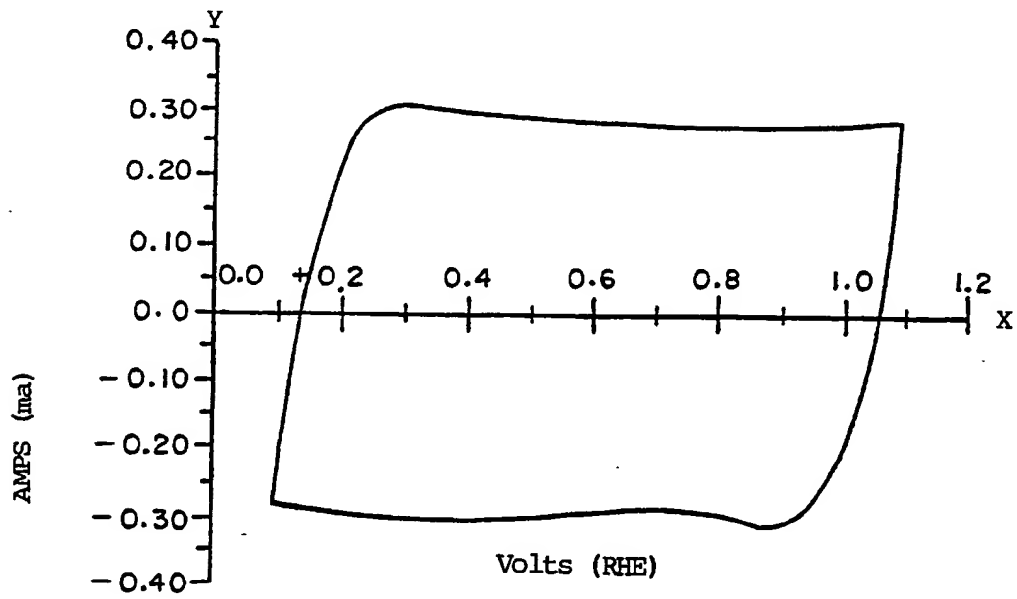


FIG. 3

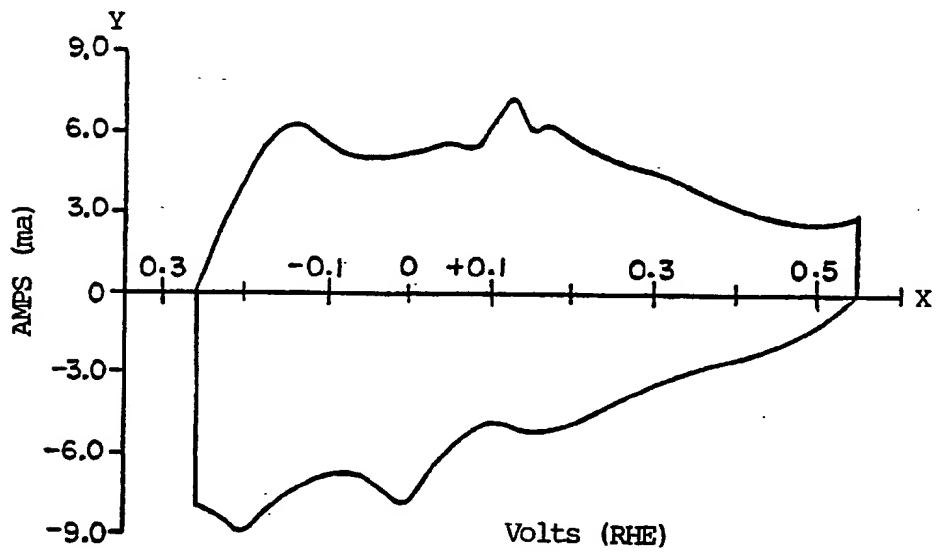


FIG. 4

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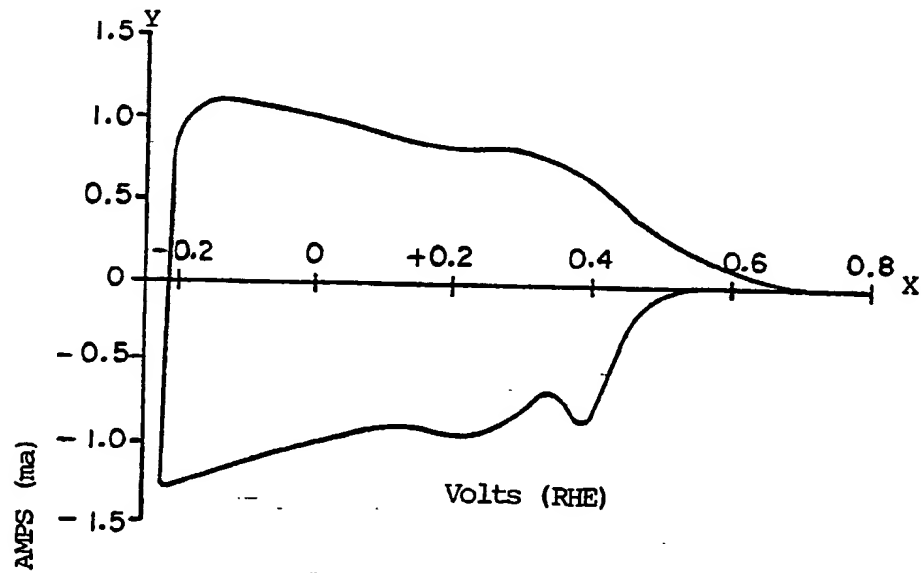


FIG. 5

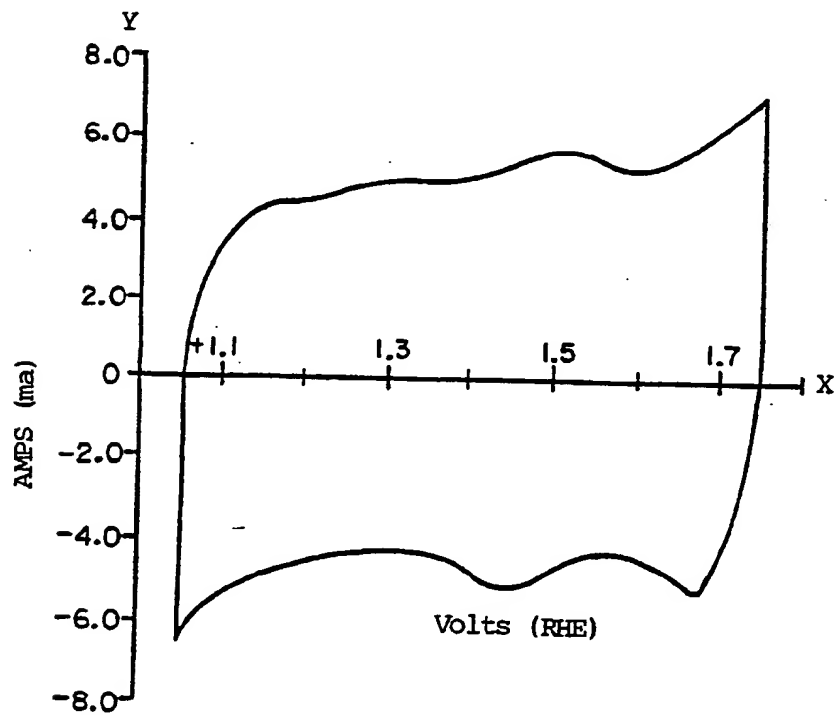


FIG. 6

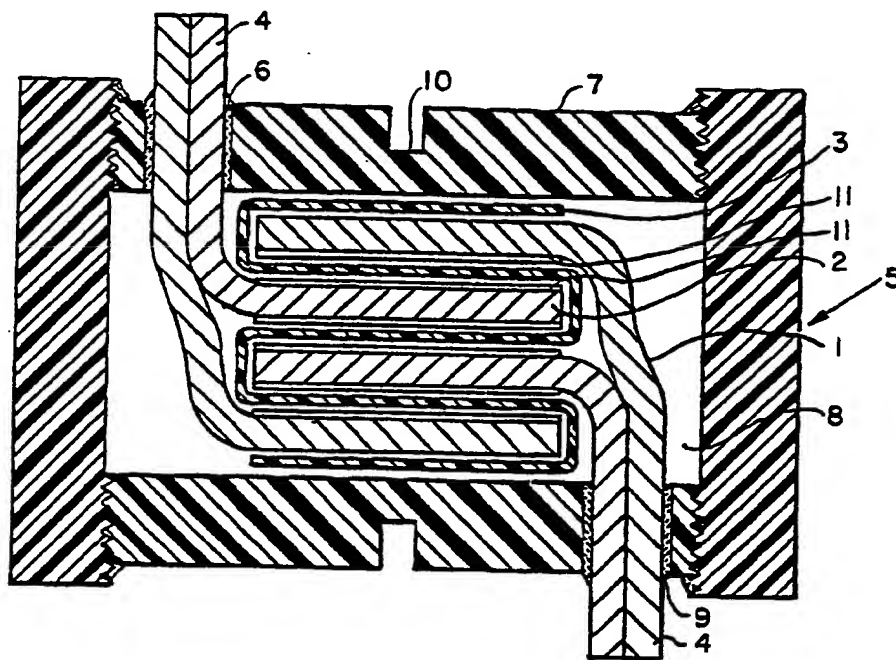
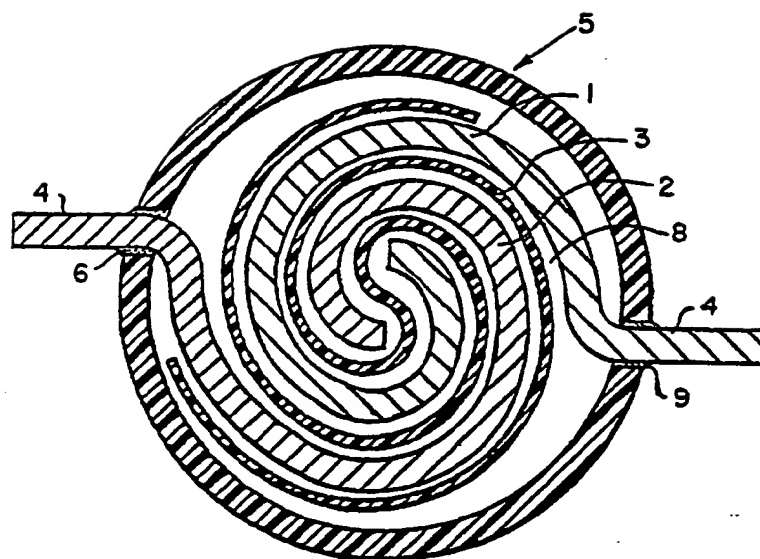


FIG. 7



**FIG. 8**

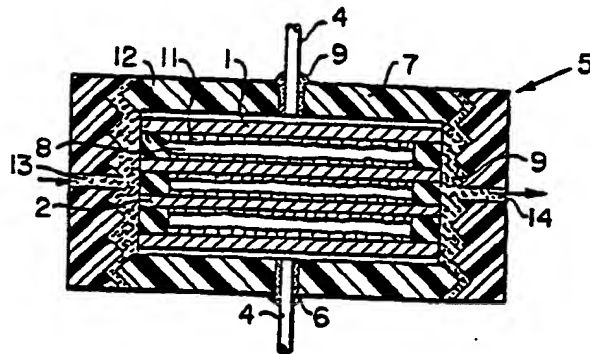


FIG. 9

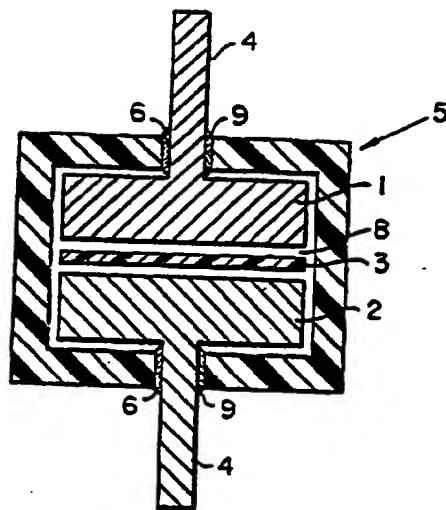


FIG. 10